

**SUBCONTRACT TITLE:** Innovative Characterization of Amorphous and Thin-Film Silicon for Improved Module Performance

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**SUBMITTED TO:** Bolko von Roedern  
National Renewable Energy Laboratory

**PRINCIPAL INVESTIGATOR:** J. David Cohen, Department of Physics  
University of Oregon, Eugene, OR 97403

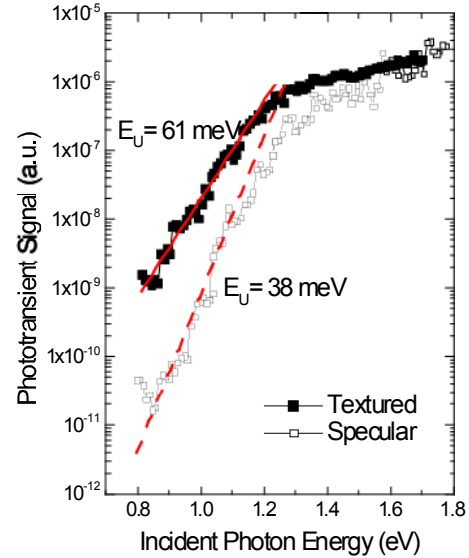
This report covers the third quarter of Phase I for the period 28 October 2005 to 27 January 2006 of the Thin Film Partnership Subcontract ZXL-5-44205-11. The primary results obtained in my laboratory during this period has focused on characterizing a series of five nc-Si:H solar cell devices that were obtained from United Solar Ovonic Corporation (USOC) in the late fall, 2005.

Whereas our earlier studies primarily employed specialized a-Si:H/nc-Si:H/a-Si:H sandwich test device structures, we have more recently been applying our capacitance-based characterization methods to a series of actual working nc-Si:H photovoltaic devices of varying efficiencies. This should allow us to more directly correlate the results of our measurements with the actual device performance parameters. The results presented in this report will concentrate on five such n-i-p devices. Two of these were deposited on specular stainless steel (SS) substrates, and three employed textured Ag/ZnO substrates. All the nc-Si:H intrinsic layers were deposited using a modified VHF glow discharge process with a thickness roughly 1.5  $\mu\text{m}$ . For all samples, ITO dots with an area of 0.05  $\text{cm}^2$  or 0.25  $\text{cm}^2$  were deposited on the p layer as top contacts. In addition, three of the samples were grown using a  $\text{H}_2$  dilution profiling process to control crystalline size and volume fraction distribution. The other two samples were grown using a constant  $\text{H}_2$  dilution process for comparison. The structures that were deposited on textured substrates were nearly identical to actual end-product devices and so constituted material tested in its optimized geometry. Indeed, as can be seen from the cell performance parameters are listed in Table I, this sample set included one sample with an efficiency that exceeded 8.5%.

**Table I.** Performance properties nc-Si:H devices examined in current study

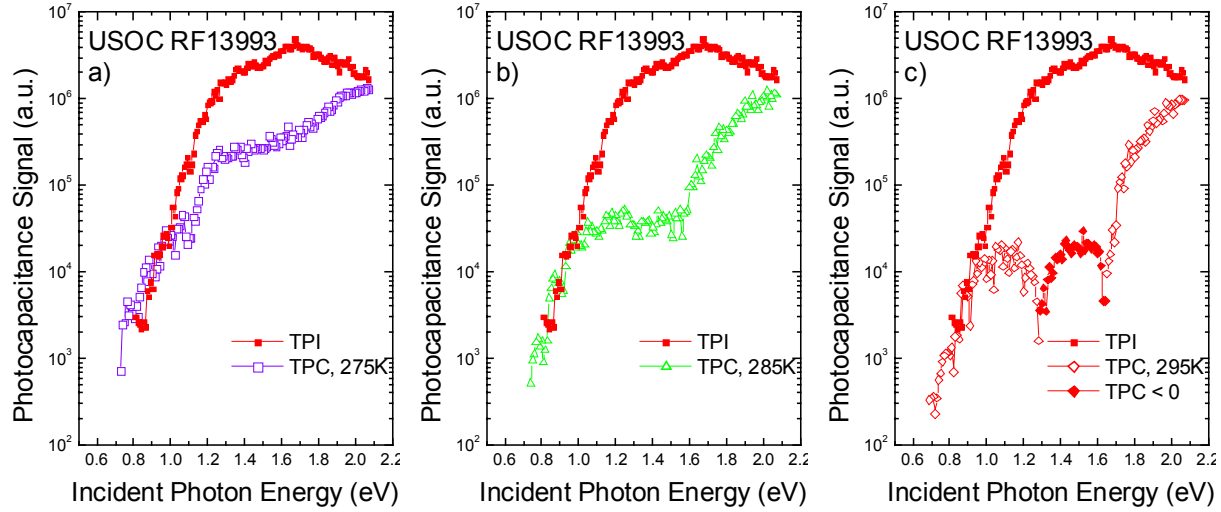
Sample No	Substrate	$J_{\text{sc}}$ ( $\text{mA}/\text{cm}^2$ )	$V_{\text{oc}}$ (volts)	FF	Eff (%)	$\text{H}_2$ Dilution
14027	Ag/ZnO	26.5	0.469	0.581	7.22	Profiling
14036	SS	17.38	0.448	0.568	4.42	Profiling
14037	Ag/ZnO	25.99	0.429	0.512	5.71	Constant
14038	SS	17.36	0.451	0.531	4.16	Constant
13993	Ag/ZnO	24.39	0.548	0.641	8.57	Profiling

**FIG 1.** TPI spectra for samples on specular (solid symbols) and textured substrates (open symbols) are aligned at the higher optical energies for comparison purposes. The flatter optical response for the textured substrate sample above 1.2 eV, as well as its apparently broader Urbach tail, are attributed to the light-trapping effect due to the textured substrate. Thus, the spectrum for the device deposited on the specular SS substrate is believed to more accurately represent the optical absorption properties of the intrinsic nc-Si:H layer itself.



It is well known that substrate texturing enhances the spectral response of a device, especially for long wavelength photons. Although substrate texturing in these samples is clearly necessary to achieve the highest conversion efficiencies, texturing also significantly modifies the spectral response that we obtain in our sub-bandgap absorption spectra, and yields a somewhat distorted representation of the optical response of the nc-Si:H film itself. Figure 1 illustrates this point by comparing two transient photocurrent spectra for one textured substrate sample device (13993) with one without texturing (14036), both deposited in a similar manner with hydrogen profiling. The textured sample's flattened TPI response above roughly 1.3 eV, and its apparently broader Urbach energy below 1.1 eV are attributed to light-trapping effects. The specular sample is thus believed to show a much less distorted picture of the actual nc-Si:H optical absorption properties.

These samples were characterized using Transient Photocapacitance (TPC) spectroscopy, Transient Photocurrent (TPI) spectroscopy, and drive-level capacitance profiling (DLCP). Figure 2 displays 1.1 kHz TPC profiles for textured sample 13993 at three different temperatures. In each case, the TPC profile is aligned with the same representative TPI spectrum of this sample for reference (the TPI spectra for a given sample exhibit nearly no temperature variation). At 275 K and 285 K, we obtain TPC spectra that agree qualitatively well with spectra we obtained in previous work [3]. At 285 K the spectra clearly exhibit the amorphous phase present in these nanocrystalline devices by showing both a distinct a-Si:H bandtail near the amorphous silicon band-gap, as well as evidence of mid-gap states at lower incident photon energies. These spectra also exhibit the previously observed temperature variation in that, by decreasing the measurement temperature by 10 K (Fig. 2a), the TPC spectrum increases by more than a factor of 10 near 1.5 eV, indicating a corresponding decrease in the net hole collection at this photon energy. An even more dramatic change is observed when the temperature is raised to 295 K in this sample: the TPC signal actually becomes slightly *negative* near 1.5 eV. The absolute value of these negative data points are plotted in solid symbols in Fig. 2c. This negative signal indicates that *more* holes are being collected than electrons at these optical energies, probably because some of the photo-excited electrons become deep trapped and cannot escape during the 500 ms time window of our measurement. Therefore, the slight negative response in this region is not in itself so important; rather, it simply reflects that some electron trapping is

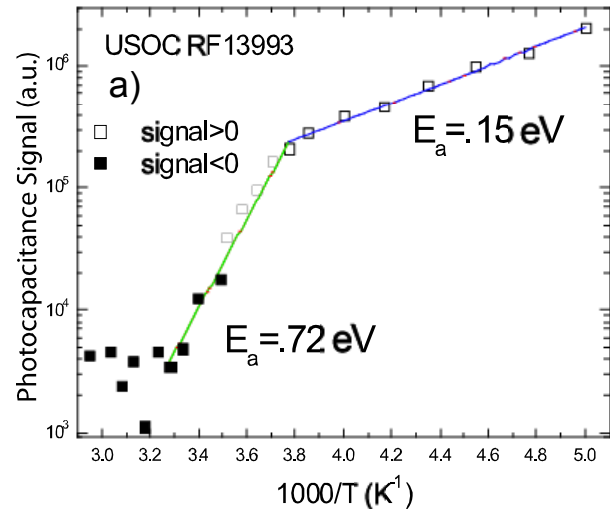


**FIG 2.** Comparison of TPI and TPC spectra at 275 K(a), 285 K(b), and 295 K(c) for the high-efficiency textured sample 13993. Nanocrystalline and amorphous phases are visible at low and high temperature, respectively. Note the negative TPC signal near 1.5 eV at 295 K.

occurring and that the hole collection is extremely good. Note that the signal again becomes positive at low optical energies since single-carrier excitation processes dominate in the deep defect region, and also positive at higher optical energies because the a-Si:H contribution with its lower hole collection fraction is larger in this region .

We examined the temperature dependence of the TPC signal in detail at an optical energy near 1.5 eV for this sample and found that the hole collection appeared to be thermally activated as shown in Fig. 3. At lower temperatures, when the hole collection was strongly suppressed, we obtained an activation energy for hole collection that was very similar to that found previously [3]. However, in the temperature regime above 270K a significantly larger activation energy near 0.72 eV was exhibited. We tentatively attribute this to hole trapping into deep defects, possibly Si dangling bonds in the amorphous component. The fact that this deeper hole trapping accounts for only about 10% of the total (by comparing the magnitudes of hole collection at 200K and 300K) seems consistent with the idea that these deeper defects reside in the phase with lesser volume fraction in these materials; that is, the amorphous phase.

**FIG 3.** Variation of TPC signal with temperature at an optical energy near 1.5eV. A positive constant was added to the TPC signal to allow these data to be plotted on a logarithmic scale (the negative region is indicated by the solid symbols). We chose the constant which best extended the exponential dependence into the regime above 270K. This graph indicates thermally activated behavior for hole collection and, in contrast with previous results showing a single activation energy near 0.2eV, this sample reveals a second regime at higher temperatures with a significantly larger activation energy.

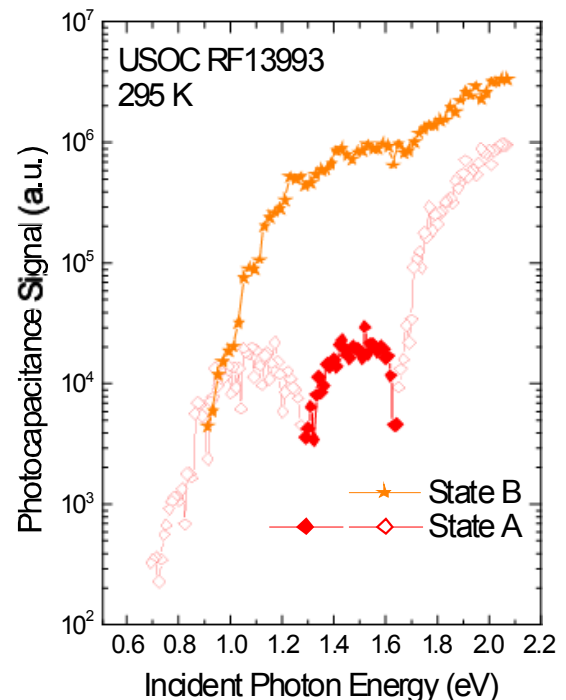


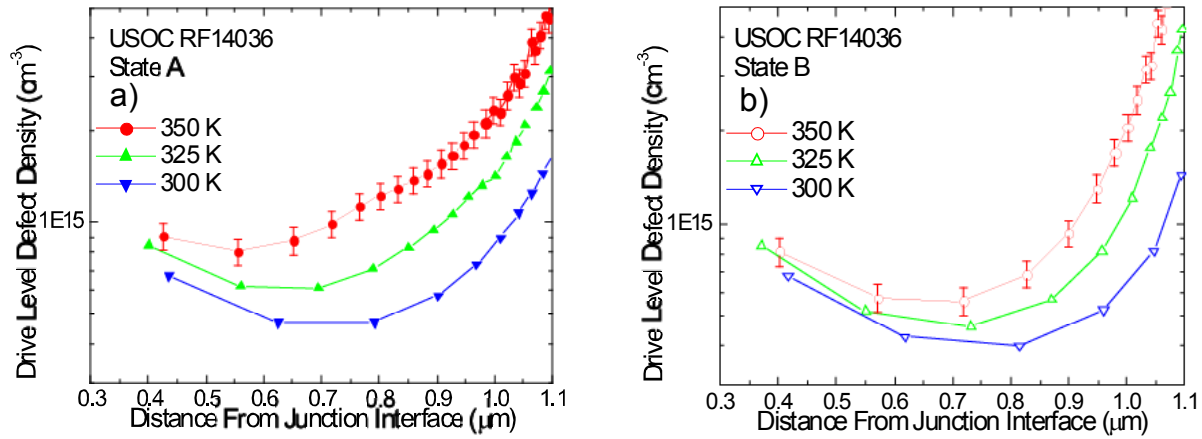
We also found that the relative hole collection was strongly sample dependent. For the three textured samples: 13993, 14027, and 14037, we determined the relative hole collection fractions at 300 K by aligning TPC and TPI spectra in the defect regime at 0.9 eV and then determining the average TPC/TPI ratio near an incident optical energy of 1.5 eV. This provided an estimate of the ratio  $(n-p)/(n+p)$ , from which the ratio  $p/n$  of collected holes relative to electrons could be determined. For the three textured samples studied, there indeed appeared to be a good correlation between the  $n/p$  collection ratios determined in this fashion and the cell conversion efficiencies. However, a much larger number of samples will need to be examined in this fashion before taking this result too seriously.

Although nc-Si:H does not suffer as severely from light exposure as amorphous silicon, prolonged light soaking typically reduces the conversion efficiency by several percent [4]. Several of our samples were examined both in “State A”, after a sample had been annealed for 1 hour at 450 K, as well as in “State B”, a degraded state which we obtained by exposing the sample to 20 hours of red-filtered light ( $>620$  nm) from a tungsten-halogen source at an intensity of  $400 \text{ mW/cm}^2$ . Effects of such light soaking could be observed both in the photo-transient spectra as well as in drive-level capacitance profiles (DLCP). The effect of light soaking on the TPC spectra of sample 13993 is shown in Fig. 4. We see that the TPC signal changes significantly. In particular, the negative signals near 1.5 eV become significantly positive in State B. This corresponds to a loss of hole collection, even more than was achieved by reducing the measurement temperature from 295 K to 275 K in State A (see Fig 2).

In numerous previous studies of light-induced degradation in a-Si:H, DLCP measurements always clearly revealed a systematic increase in the density of deep defects, by factors varying from roughly 2 to almost 50.[6,7] However, our previous DLCP studies for nanocrystalline materials indicated almost no change.[8] and, moreover, very little evidence for a deep defect thermal response at all. In contrast, for some of the current series of nc-Si:H devices,

**FIG 4.** Comparison of the 295K TPC spectra for sample 13993 before and after light-soaking. We see an dramatic increase in the magnitude of the TPC spectrum, especially in the regime where the annealed state had exhibited a negative TPC signal. This is due to a substantial reduction in the minority carrier collection.

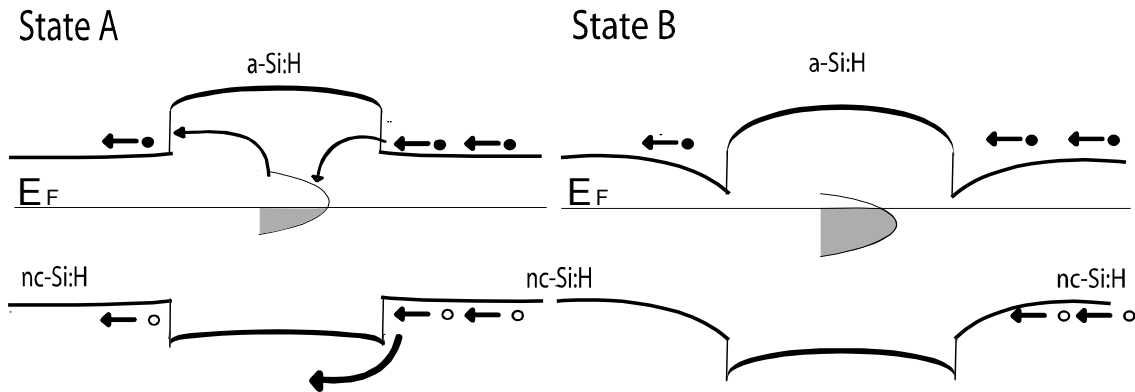




**FIG 5.** 1.1 kHz DLCP profiles obtained for a series of temperatures for both (a) the annealed State A and (b) light-soaked State B of one nc-Si:H sample deposited on specular stainless steel. The increasing density with temperature is due to the response of deep defects. However, this response from the deep defects actually appears to be reduced after light soaking. Representative errors are shown in for the 350K spectrum in each case.

particularly for samples 13993 and 14036, the DLCP measurements have revealed a significant deep defect response, as is illustrated in Fig. 5. This may partly be due to the smaller effective doping levels in these samples which allow us to more clearly observe the contribution from the deep defects. What is particularly surprising, however, is that when such a deep defect response is apparent, we consistently have found that it *decreased* after prolonged light exposure, as illustrated in Fig. 5b.

To explain the observed effects of light-soaking on the DLCP and TPC measurements, we tentatively propose a microscopic degradation model. First, we note that that DLCP density represents the integral over the density of states in the gap between the Fermi level and a thermal response energy. Thus, the observed decrease in drive level density may result from defects effectively “shifting out” of the energy region defined by our DLCP measurement parameters. At the same time, the observed reduced hole-collection implies an impediment to hole transport.



**FIG 6.** Schematic of a possible model to explain light-induced changes observed in the drive-level profiles and the photocapacitance spectra. In State B, defects have shifted down in energy with respect to the bulk conduction band and holes see a larger potential barrier at the phase boundary. In the scenario illustrated, positive charge has collected at the a-Si:H/crystallite interfaces, and is compensated by negative charge in the a-Si:H region, as well as in the crystallite nearby.

Both of these observed effects could result from of a shift in the potential distribution between the nanocrystallites and amorphous regions of these mixed phase materials, as shown in Fig. 6. Such a shift in the relative potentials of the two phases might occur during light-soaking by a separation of the photo-generated charges, with positive charge accumulating at the amorphous-nanocrystalline phase boundary, and compensating negative charge being added to the dangling bond defects within the amorphous regions. Future studies have begun to test some of the other possible implications of such a microscopic model.

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